Element Concentrations in the Fossil Bones Using Neutron Activation

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University of Toronto

In this paper we present the results of preliminary Neutron Activation analyses of fossil bone samples from the Old Crow River region of the Northern Yukon Territory, Canada. This region, shown on the first SLIDE (1), is of particular interest to pal[illegible] archaeologists because it remained unglaciated during the Pleistocene glacial periods and hence served as a refugium for flora and fauna (perhaps including early man) at a time when most of northern North America was covered by heavy ice sheets.

Although the area is now underlain by permafrost, downcutting by the Old Crow River has exposed local stratigraphy in several localities. Large numbers of vertebrate fossil bones are found in secondary and tertiary alluvial deposits in the river bluffs and on the river banks and bars. Carbon 14 dating indicates that the majority of bones are more than 22,000 years old. Faunal evidence indicates that most of the bones recovered may be attributed to Wisconsin time, but some are of Sangamon age and a few are of Early and Middle Pleistocene age. In general the b [illegible] varying shades of brown. Dr. W.N.Irving [illegible] ny of the bones were deposited in wat [illegible] idence suggests that many animals may [illegible] n the ice of ponds and lakes. On thawing, the bones sank to the bottom of these lakes, where they were incorporated in sediments, mineralized, and later protected from bacteri attack and mechanical attrition by freezing of the sediments. Erosional proc eventually re-exposed the bones and fluvial action subsequently (and in many cases relatively recently) transported them to sites from which they were recovered. Many other bones show evidence of substantial root etching indica that they had lain on or near ground surface for a considerable time before being deposited in primary sediments.

Fossil bones are known to accumulate minerals from percolating ground water and to exchange elements with their surroundings. It occurred to us that measurements of elemental concentrations in these fossils would provide a quantitative figure for the extent and nature of the mineralization. It mi also be possible to discern multiple mineralization events, and to [illegible] [illegible] in the long, cold history of these bones, the mineralizat[illegible] took pl

[illegible]RP Contribution No. 10 - (Abstract published in Proc)

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In this paper we present the results of preliminary Neutron Activation analyses of fossil bone samples from the Old Crow River region of the Northern Yukon Territory, Canada. This region, shown on the first SLIDE (1), is of particular interest to palaeontologists, palaeobotanists and archaeologists because it remained unglaciated during the Pleistocene glacial periods and hence served as a refugium for flora and fauna (perhaps including early man) at a time when most of northern North America was covered by heavy ice sheets.

Although the area is now underlain by permafrost, downcutting by the Old Crow River has exposed local stratigraphy in several localities. Large numbers of vertebrate fossil bones are found in secondary and tertiary alluvial deposits in the river bluffs and on the river banks and bars. Carbon 14 dating indicates that the majority of bones are more than 22,000 years old. Faunal evidence indicates that most of the bones recovered may be attributed to Wisconsin time, but some are of Sangamon age and a few are of Early and Middle Pleistocene age. In general the bones are very well preserved and stained varying shades of brown. Dr. W.N.Irving and his colleagues have suggested that many of the bones were deposited in water soon after the death of the animals. Evidence suggests that many animals may have been killed and dismembered by Man on the ice of ponds and lakes. On thawing, the bones sank to the bottom of these lakes, where they were incorporated in sediments, mineralized, and later protected from bacterial attack and mechanical attrition by freezing of the sediments. Erosional processes eventually re-exposed the bones and fluvial action subsequently (and in many cases relatively recently) transported them to sites from which they were recovered. Many other bones show evidence of substantial root etching indicating that they had lain on or near ground surface for a considerable time before being deposited in primary sediments.

Fossil bones are known to accumulate minerals from percolating ground water and to exchange elements with their surroundings. It occurred to us that measurements of elemental concentrations in these fossils would provide a quantitative figure for the extent and nature of the mineralization. It might also be possible to discern multiple mineralization events, and to determine when in the long, cold history of these bones, the mineralization took place.

NYRP Contribution No. 10 - (Abstract published in Proc)

A number of investigations of the chemical composition of fossil bones have been reported, but few of these have used neutron activation analysis, and none, as far as we are aware, have examined the extent to which the concentration in a given bone may vary with depth below the bone's surface.

A representative set of bones was selected for analysis from the Northern Yukon Research Programme collection. These are shown in the next SLIDE (2). [Note the wide range of surface colouration, black to pale brown; several complete bison bones are included, as well as fragments of a humerus, a proboscidea long bone, and a modern moose bone].

In the next SLIDE (3), which is a picture of a core drilled from the shaft of one of the bones, it is clear how superficial the staining is on these bones.

The next SLIDE (4) indicates how the bones were sampled. Each specimen was positioned under a vertical rotary drill press, and a set of three end mills of successively smaller diameter [9.53 mm, 7.93 mm, and 6.35 mm] were used to drill out a sequence of samples of increasing depth. End mills were used so that the depth range of each sample relative to the bone surface was reasonably well defined. The sequence of mills of decreasing diameter was necessary to minimize the possibility of contaminating deeper samples with surface bone. Thickness of each sample was measured using a caliper.

Amounts of the powdered samples obtained in this way varied from 32 milligrams to 400 milligrams depending on depth and bone density. The sequence of samples taken penetrated close to, or into the hollow interior of the bone shaft in all cases, with the exception of the proboscidea fragment.

The weighed samples were placed in polyethylene capsules, and irradiated in the Slowpoke nuclear reactor facility at the University of Toronto. Three separate irradiations were undertaken at intervals of several weeks, the first for 2 minutes at a 2 kilowatt power level, the second for 10 seconds at the same power level, and the third for 16 hours at 2 kilowatts. After suitable delays the gamma activities of the samples were determined using a lithium-drifted germanium detector and a Canberra multi channel analyser.

Gamma counts were converted to parts per million, or percent, with the aid of factors determined for separated pure elements and provided to us by Dr. R.G.V. Hancock of the Slowpoke Facility.

For Bone samples in the range of 150 to 200 milligrams, Manganese, iron, sodium, aluminum and calcium can be determined at the concentration levels at which they occur, with better than plus or minus a few percent statistical error; magnesium, barium, vanadium, zinc, scandium and cobalt with about plus or minus ten percent error; uranium, fluorine and strontium with better than twenty percent error. Other elements such as chromium, thorium, dysprosium, samarium, europium and chlorine can be detected, but only measured with reasonable accuracy when their abundances are much higher than the average level in the bones.

Among the elements determined, calcium, magnesium, strontium, sodium, and zinc showed small variations within a given bone, but no obvious dependence on depth into the bone shaft. Average concentrations for these are listed on the next SLIDE (5). Calcium is a major component of the inorganic bone matrix, and it is not surprising that its concentration is the same, among all the bones. The calcium occurs as micro-crystalline hydroxy-apatite (a hydrated calcium phosphate) and the crystals of this mineral provide sites at which chemical replacement may occur, and also large surface areas on which other cations can be absorbed.

It has been suggested that the magnesium in bones may be adsorbed on these apatite crystals and may also occur in voids and channels in the bone. There are slight differences in magnesium content among the complete bison bones, but the fragmented samples [the last two under magnesium on SLIDE (5)] are much lower, suggesting that their fractured state may have facilitated a loss of magnesium. Interestingly, the fragmented samples are significantly higher in strontium than the complete bison bones, which may be a further indication of the relative ease with which exchange of magnesium and strontium may take place if internal bone surfaces are exposed by fracturing. It seems unlikely, in view of the heavily mineralized state of bones at Old Crow, and the relatively low statistical accuracy with which we are able to determine strontium by neutron activation, that it will be possible to reconstruct food chains from strontium contents in the way that has been done for other fossil animals.

Sodium concentrations in the fossils are consistent but substantially lower than that in the modern moose bone, an effect which has been documented by other workers, and attributed to leaching of sodium from apatite crystal surfaces. The zinc concentration in all the bones, fossil as well as modern, is remarkably high (about 120 parts per million) and is relatively constant with depth within individual samples. This observation suggests that the zinc was incorporated into inorganic bone-matrix when the animals were alive. As far as we are aware, zinc has not been previously observed in bones, and further analyses will evidently be necessary to check this.

In contrast to the data described so far, a number of element concentrations vary markedly and systematically with depth into the bone shafts. The series of slides which follow will illustrate this.

The next SLIDE (6) is a plot of concentration of manganese and iron as a function of depth below the outer surface at one point on the shaft of a complete fossil bison humerus. The manganese content drops from an average of 420 parts per million in the outer 1.2 millimeters of the bone to less than 50 parts per million about midway through the shaft, but rises again as the hollow interior of the bone is approached, reaching an average of 730 parts per million in the deepest 2.4 millimeter section sampled. [Note that the lines joining the points on this and subsequent slides are designed mainly to guide the eye of the observer.] Iron shows a similar kind of variation, from .5 percent on the outside of the bone, through .25 percent midway, to 1 percent close to the hollow interior. Throughout the modern moose bone, manganese is less than 4 parts per million, and iron less than .06 percent.

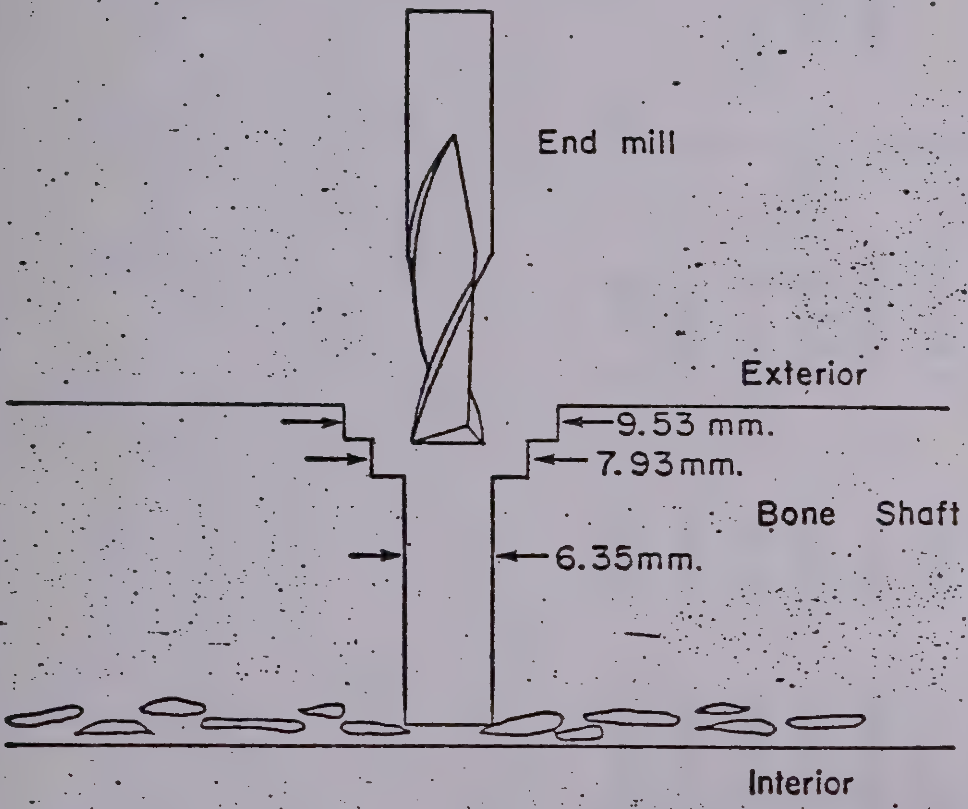
This concentration distribution is typical of all of the fossil bison humeri as are indicated by the next SLIDE (7) (pause), the next SLIDE (8) (pause) and the next SLIDE (9) (pause). It is a distribution apparent also for vanadium, of which the next SLIDE (10) is typical. [The vanadium content of modern moose bone is not detectable]. Uranium and fluorine also demonstrate this variation, as the next SLIDE (11) shows: In each case the uranium and fluorine contents of modern bone are less than 0.4 parts per million and .06 counts per milligram, respectively. [Fluorine contents are expressed in this way pending calibration of the gamma activity with pure samples of known fluorine content]. Barium concentrations follow a similar trend, but variations are less pronounced, as the next SLIDE (12) indicates.

The fragment of proboscidea long bone shows decreases in concentration inward; the next SLIDE (13) illustrates this. The iron content of the surface of this bone is the highest we have measured (4.7%) and is consistent with the bone's black colour. The next SLIDE (14), which shows the variation in uranium and fluorine contents is unusual in that the maximum uranium content occurs in the depth range .6 mm to 1.5 mm, rather than in the surface layer.

Concentration distributions in a fossil bison metacarpal do not conform to the patterns we have observed so far. The next SLIDE (15) shows the manganese and iron data for this bone. Iron has the normal distribution, but manganese has a relatively high concentration in the middle sections of the shaft sequence of samples. This distribution also shows up in the uranium and fluorine data, in the next SLIDE (16), where the middle section concentrations are higher than the exterior or interior surface concentrations.

Other workers have suggested that iron, manganese, vanadium and barium occur in minute cracks and voids in the bone structure. Our data are consistent with this, but it is not clear whether the concentration variations we observe simply reflect the distribution of voids and cracks in the bones or whether a time-dependent transfer of elements into the bone matrix from the exterior (and the interior) of the bone shafts has taken place. Whatever the process, it appears that uranium, fluorine, scandium, and chromium, participate in it. So also do dysprosium, samarium and europium, although our results show the latter three elemental variations less clearly. Experiments are being planned in an effort to decide which of these alternatives is correct, and it seems clear that neutron activation analysis will continue to play an important role in these measurements.

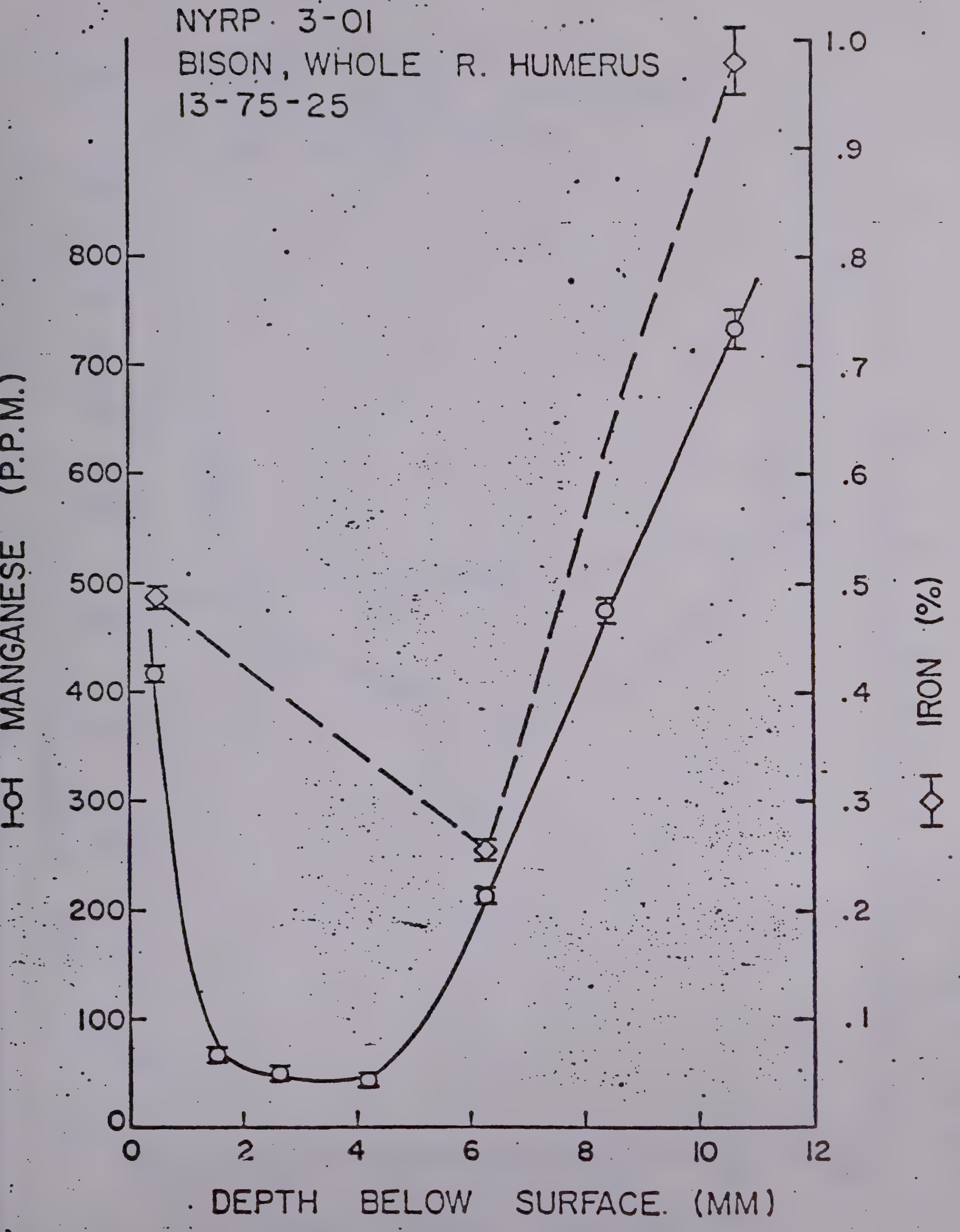
Bone sampling procedure

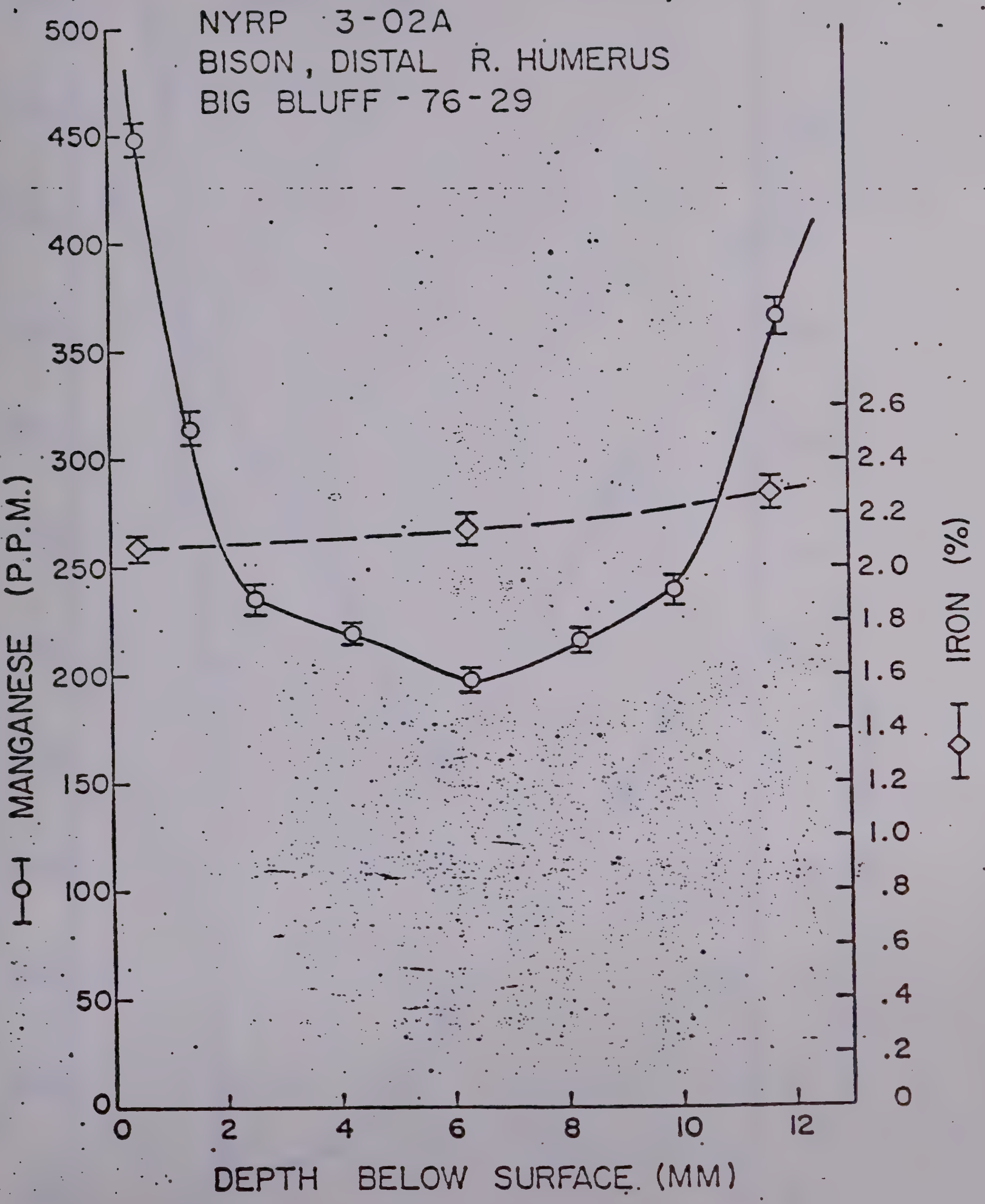


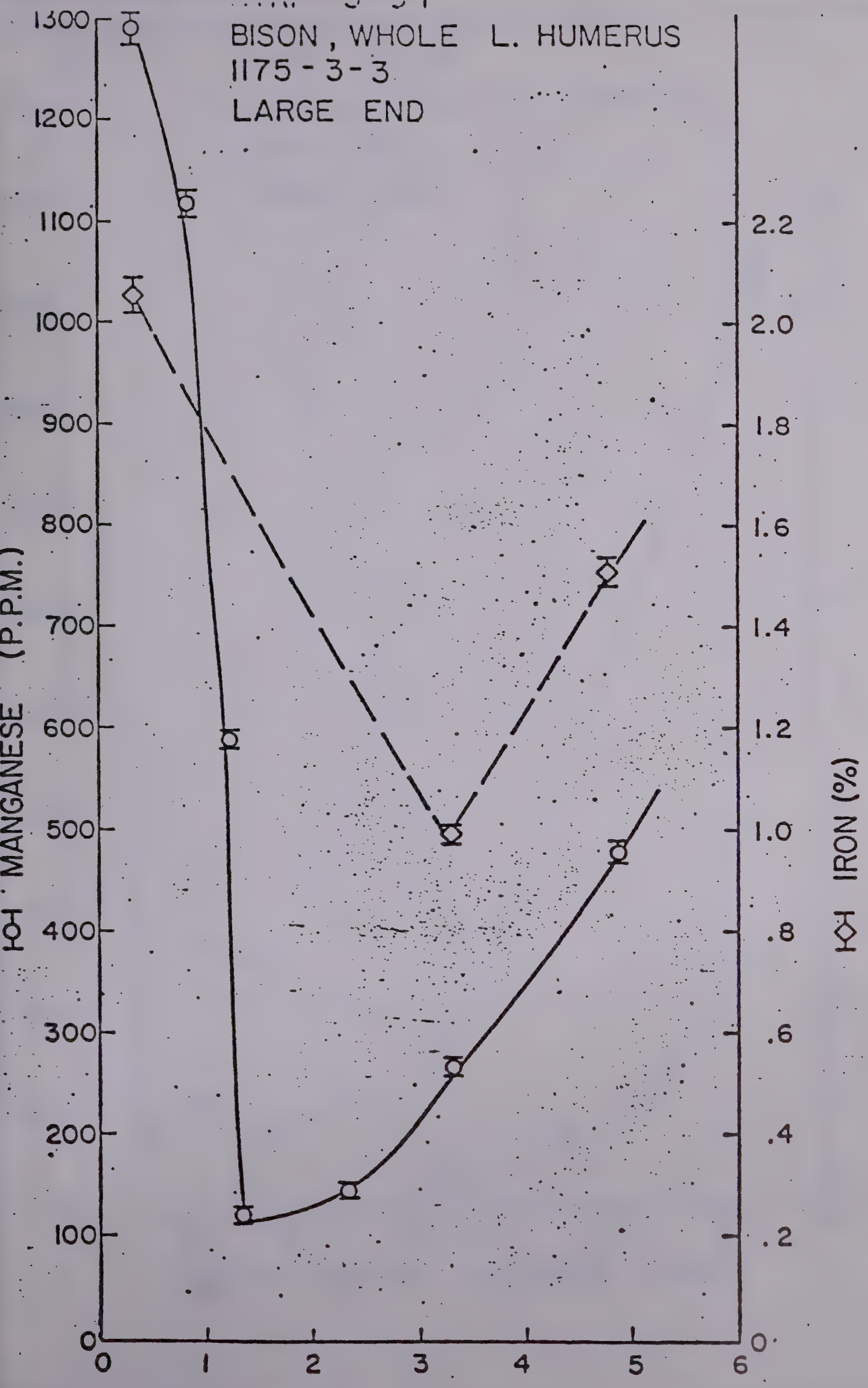
N.A.A. ANALYSES, NYRP FOSSIL BONES

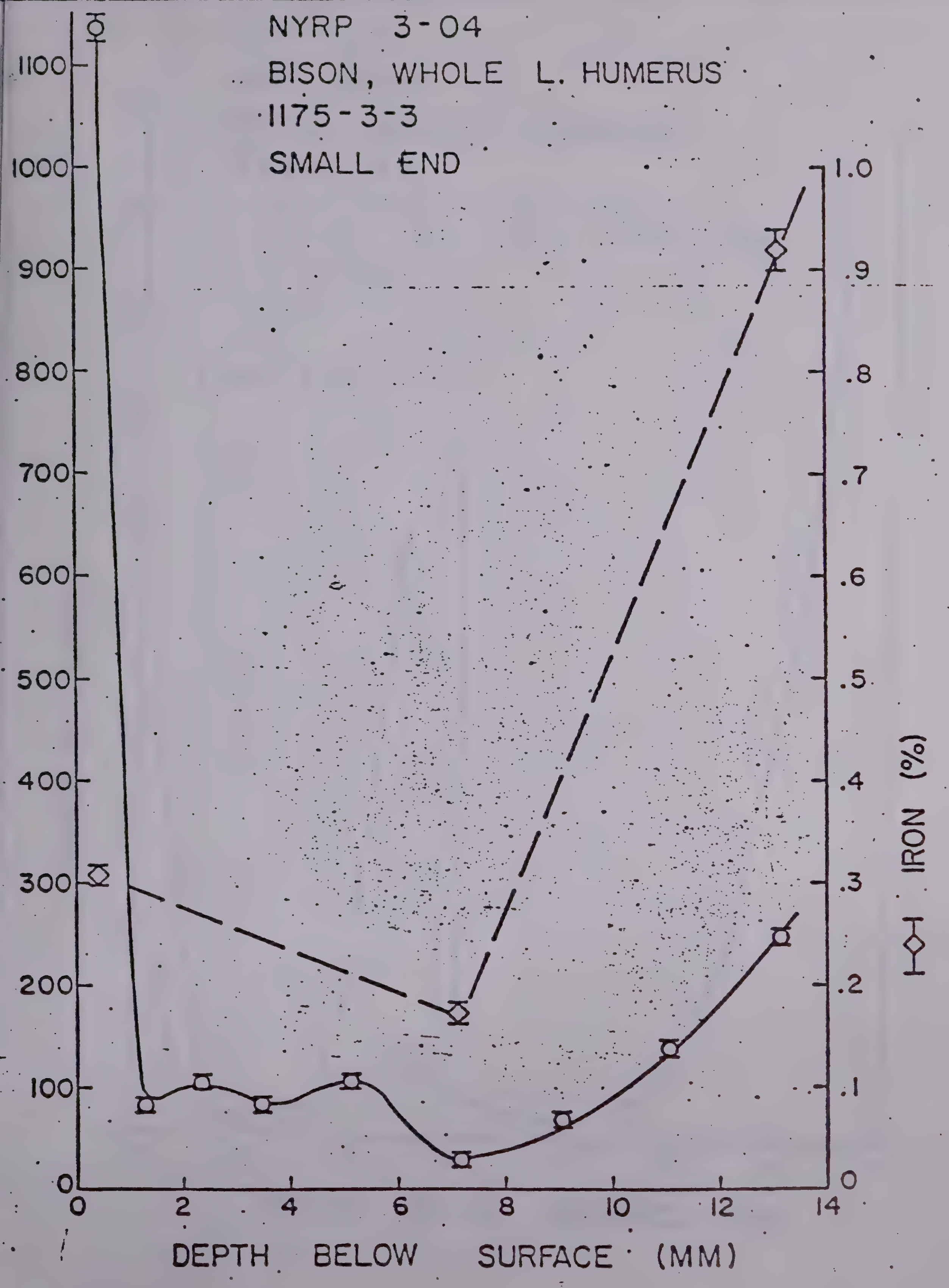
ELEMENTS SHOWING NO DEPTH DEPENDENCE

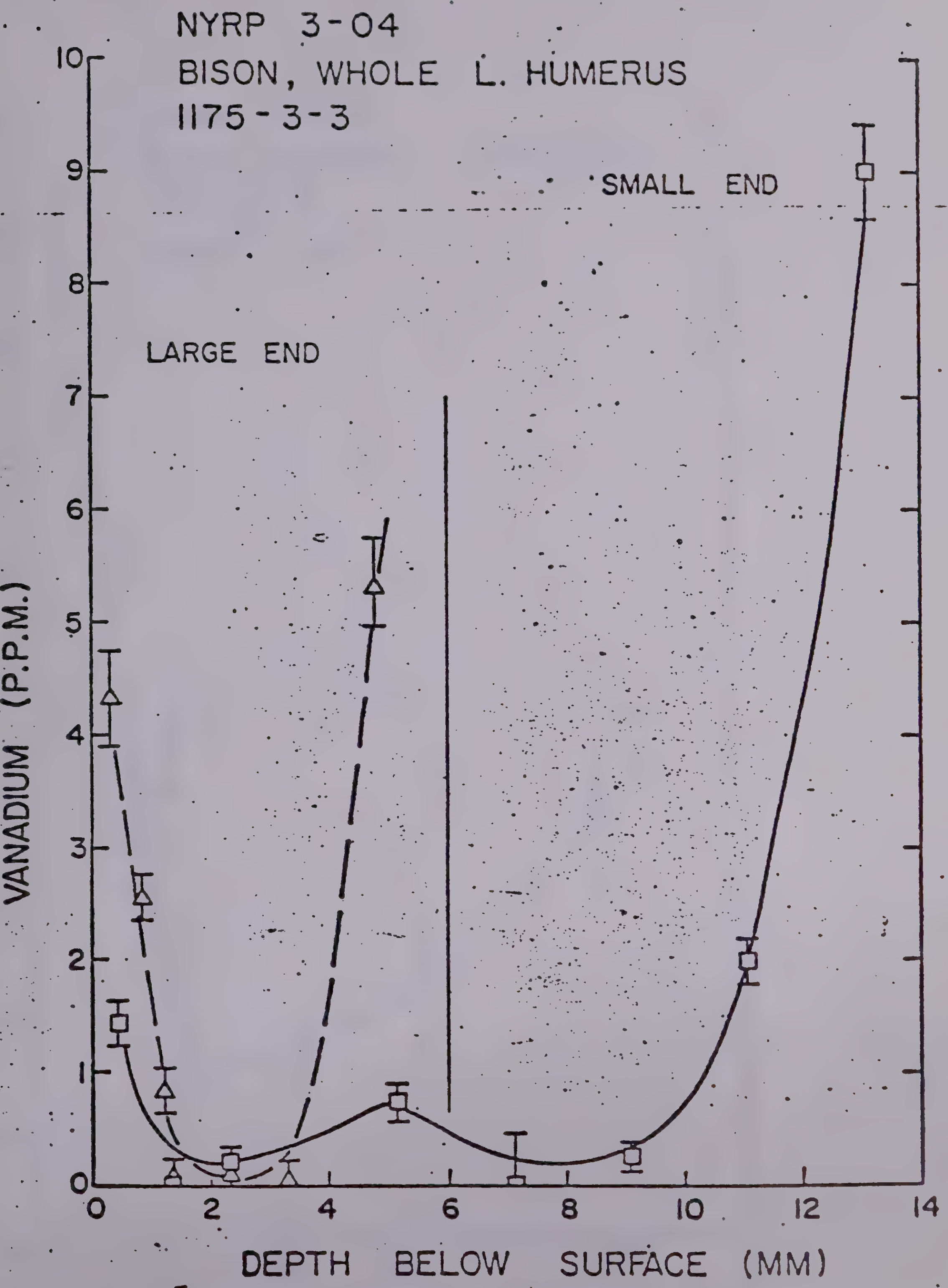
SAMPLE	N	Ca%	Mg%	Sr%	Na%	Zn%
MOOSE (MODERN, FRAGMENT)	6	27.8±1.1	.35±.05	.011±.009	.52±.06	.013±.006
3-01 (BISON, WHOLE)	7	25.6±2.1	.32±.04	.031±.011	.35±.03	.010±.003
3-04 (BISON, WHOLE, SMALL END)	9	25.4±1.2	.26±.04	.018±.014	.36±.04	.013±.004
3-04 (BISON, WHOLE, LARGE END)	7	26.1±1.5	.23±.02	.024±.012	.37±.02	.013±.001
M-01 (BISON, WHOLE)	8	24.7±1.0	.33±.07	.018±.016	.32±.05	.013±.009
3-02A (BISON, FRAGMENT)	8	25.1±1.0	.14±.02	.045±.006	.33±.01	.010±.003
M-02 (PRODOSC., FRAGMENT)	11	26.5± .8	.06±.03	.065±.014	.34±.01	.012±.004

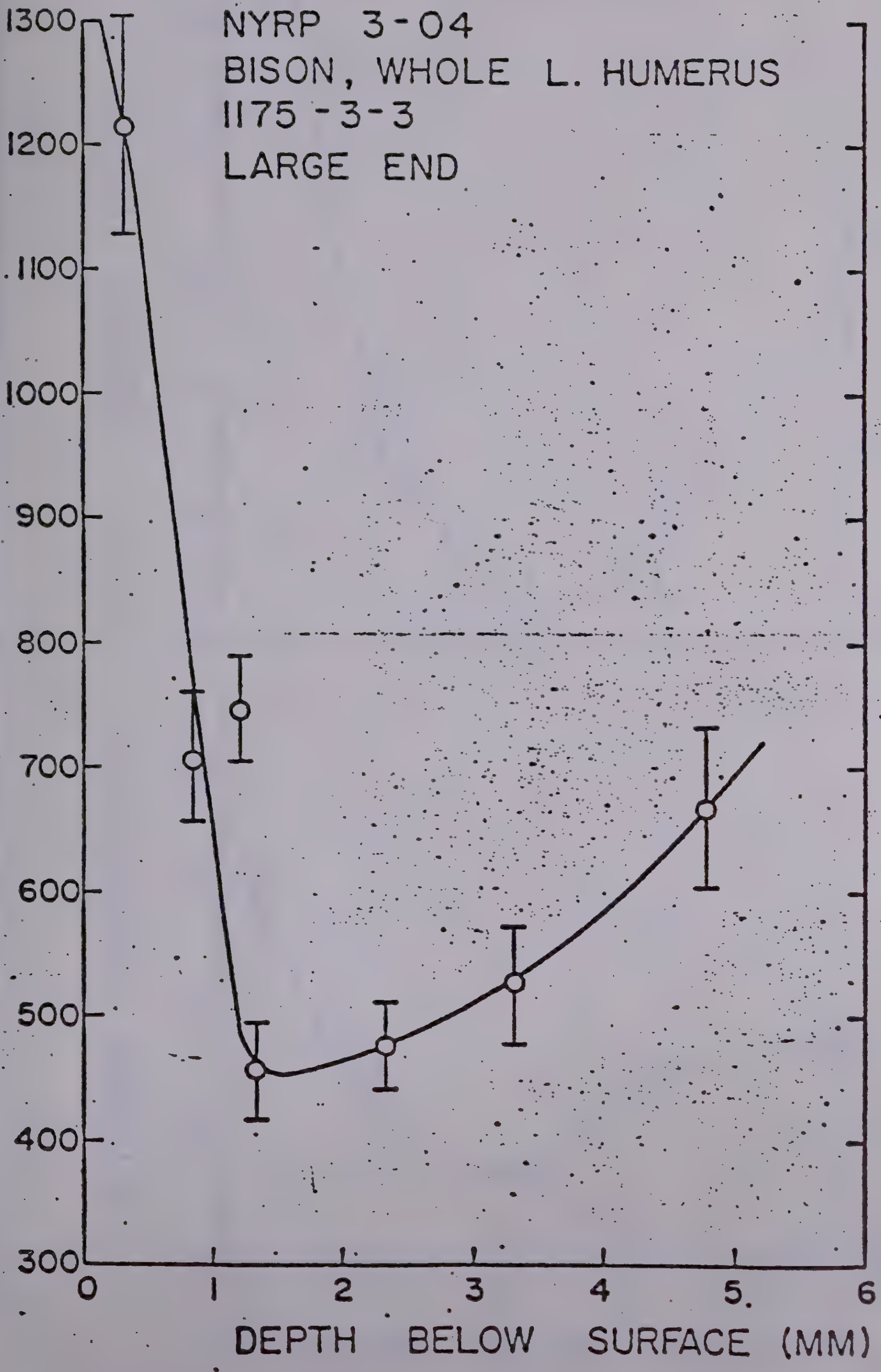

NYRP 3-01
BISON, WHOLE R. HUMERUS
13-75-25
MANGANESE (P.P.M.)
0
100
200
300
400
500
600
700
800
IRON (%)
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
0
2
4
6
8
10
12
DEPTH BELOW SURFACE (MM)

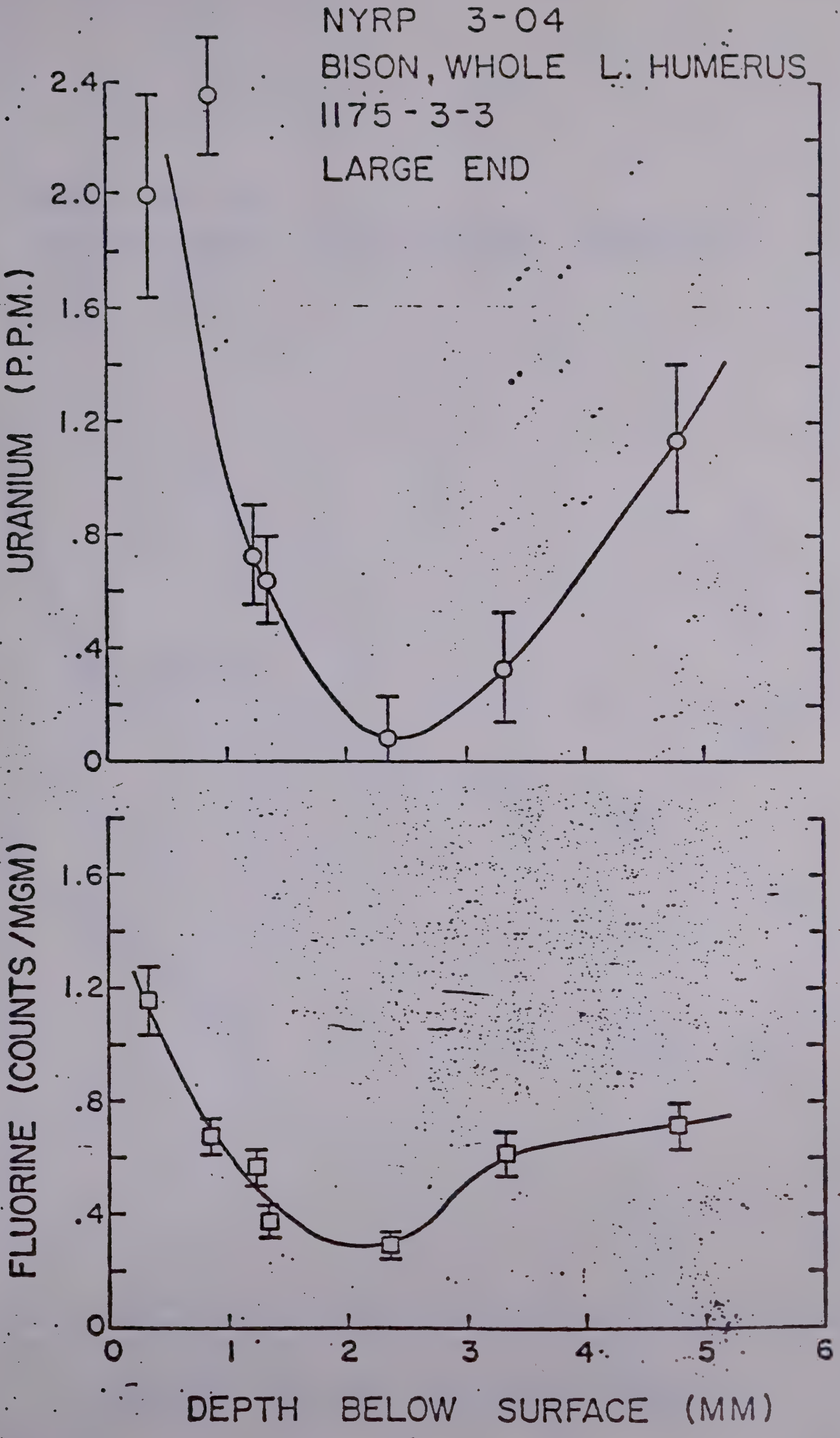

NYRP 3-02A
BISON, DISTAL R. HUMERUS
BIG BLUFF - 76 - 29
MANGANESE (P.P.M.)
IRON (%)
DEPTH BELOW SURFACE (MM)
500
450
400
350
300
250
200
150
100
50
0
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0
2
4
6
8
10
12

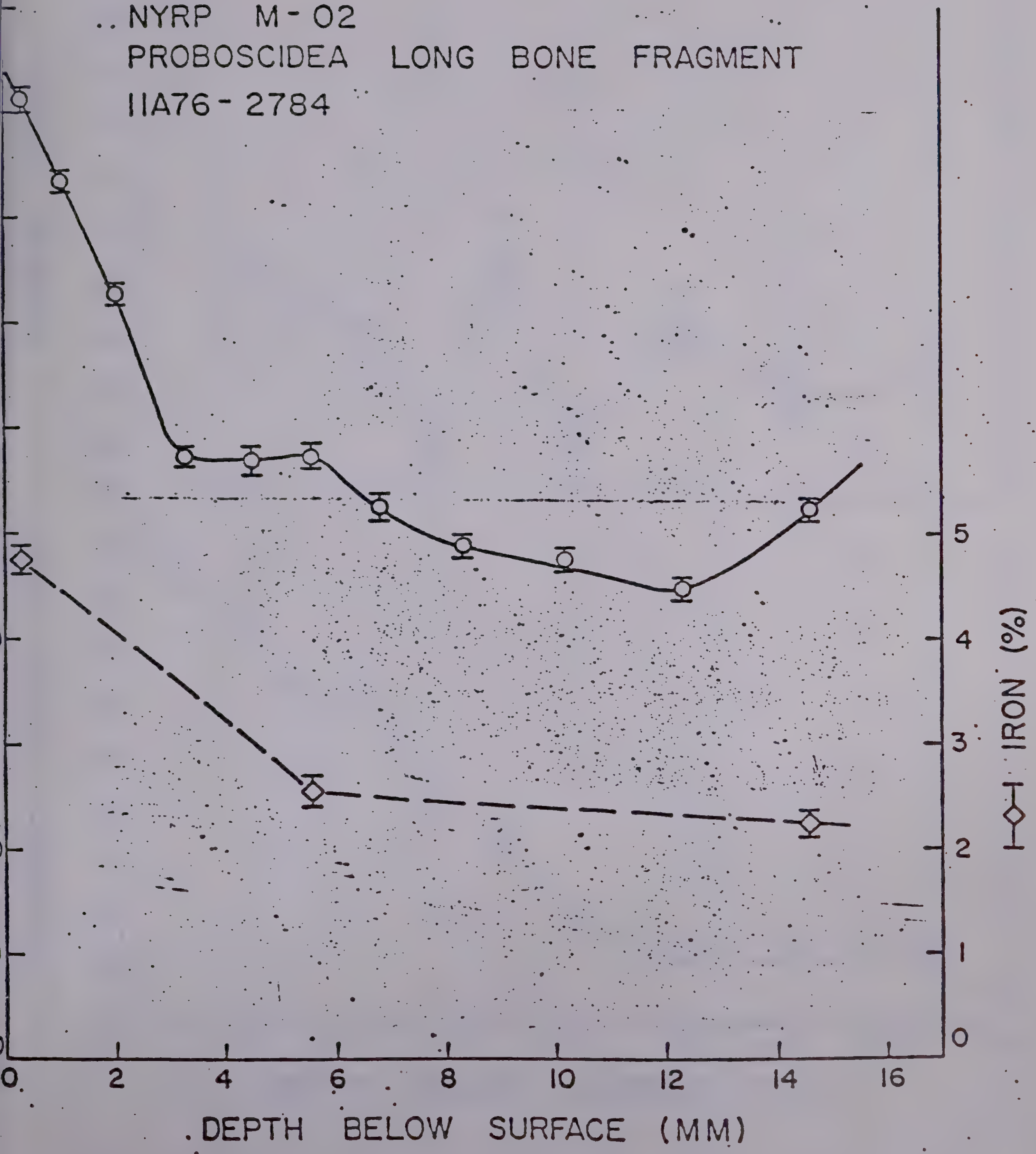

BISON, WHOLE L. HUMERUS
1175 - 3 - 3
LARGE END
MANGANESE (P.P.M.)
IRON (%)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0
1
2
3
4
5
6

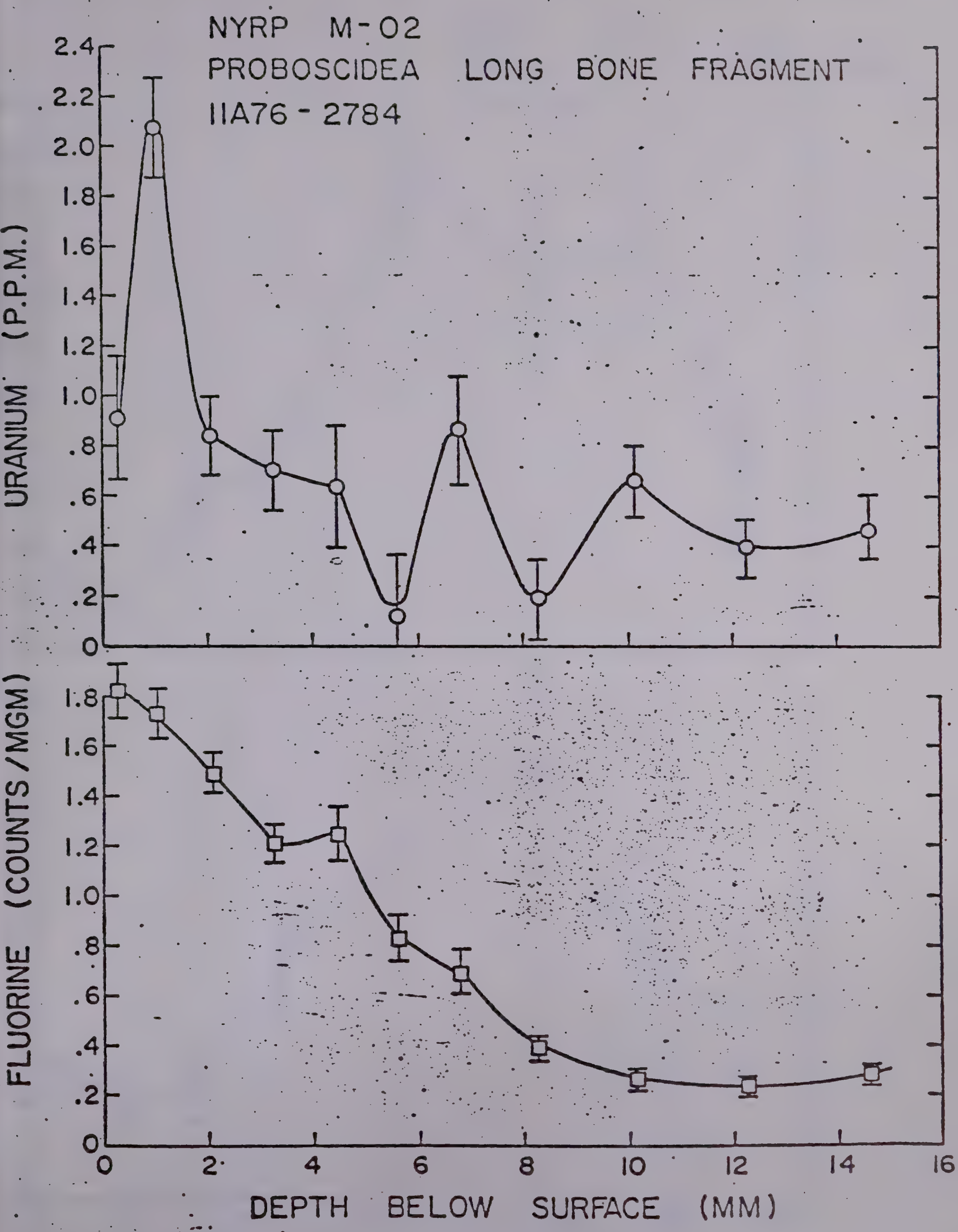

NYRP 3-04
BISON, WHOLE L. HUMERUS
1175-3-3
SMALL END
1100
1000
900
800
700
600
500
400
300
200
100
0
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
IRON (%)
0
2
4
6
8
10
12
14
DEPTH BELOW SURFACE (MM)

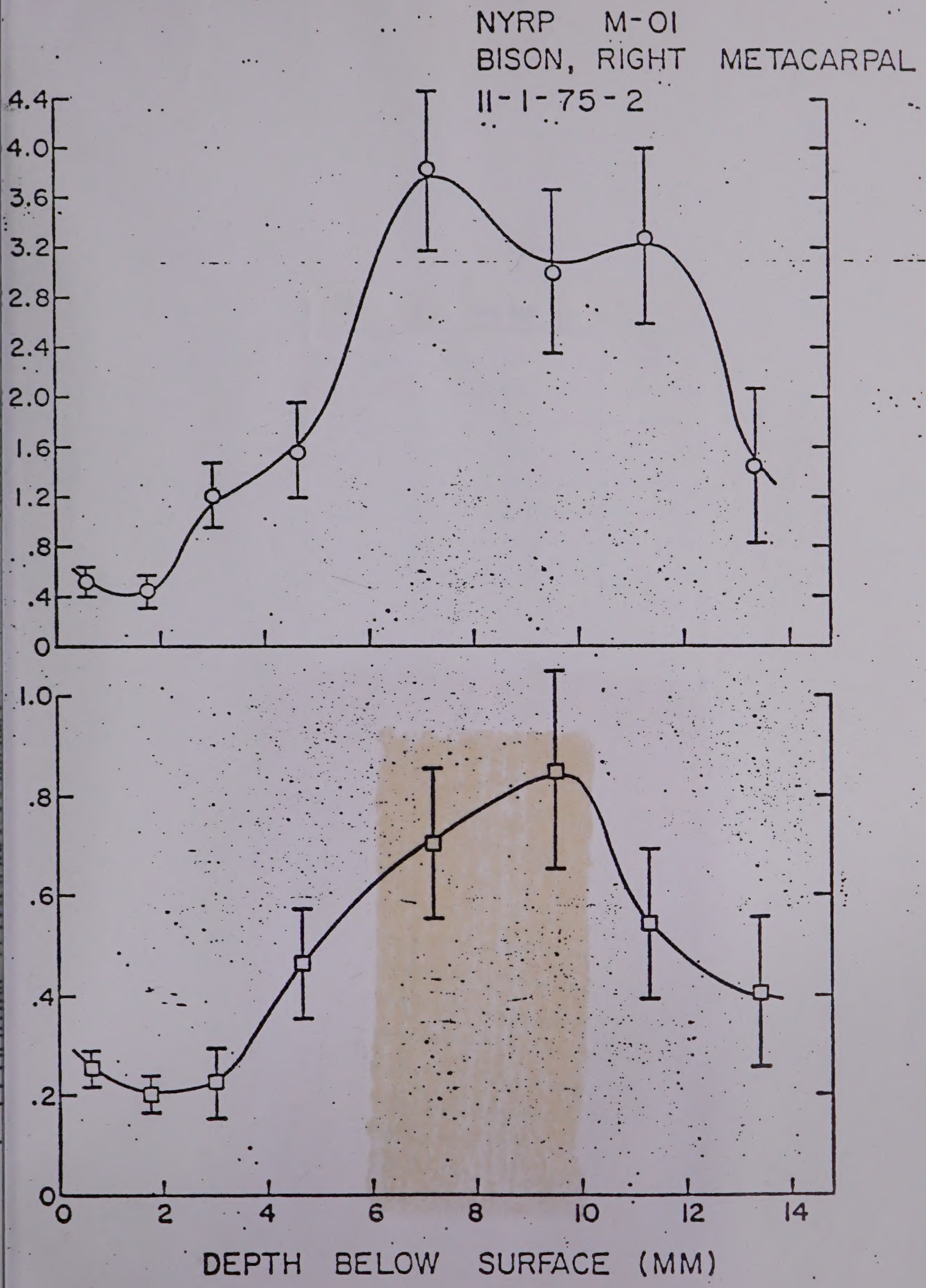

NYRP 3-04
BISON, WHOLE L. HUMERUS
1175-3-3
SMALL END
LARGE END
VANADIUM (P.P.M.)
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10
12
14
DEPTH BELOW SURFACE (MM)


NYRP 3-04
BISON, WHOLE L. HUMERUS
1175-3-3
LARGE END
1300
1200
1100
1000
900
800
700
600
500
400
300
0
1
2
3
4
5.
6
DEPTH BELOW SURFACE (MM)


NYRP 3-04
BISON, WHOLE L. HUMERUS
1175-3-3
LARGE END
URANIUM (P.P.M.)
2.4
2.0
1.6
1.2
.8
.4
0
FLUORINE (COUNTS/MGM)
1.6
1.2
.8
.4
0
0
1
2
3
4
5
6
DEPTH BELOW SURFACE (MM)


NYRP M-02
PROBOSCIDEA LONG BONE FRAGMENT
11A76-2784
0
2
4
6
8
10
12
14
16
DEPTH BELOW SURFACE (MM)
0
1
2
3
4
5
IRON (%)


NYRP M-02
PROBOSCIDEA LONG BONE FRAGMENT
11A76 - 2784
URANIUM (P.P.M.)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
FLUORINE (COUNTS/MGM)
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0
2
4
6
8
10
12
14
16
DEPTH BELOW SURFACE (MM)


NYRP M-01
BISON, RIGHT METACARPAL
11-1-75-2
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
0
1.0
.8
.6
.4
.2
0
0
2
4
6
8
10
12
14
DEPTH BELOW SURFACE (MM)

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